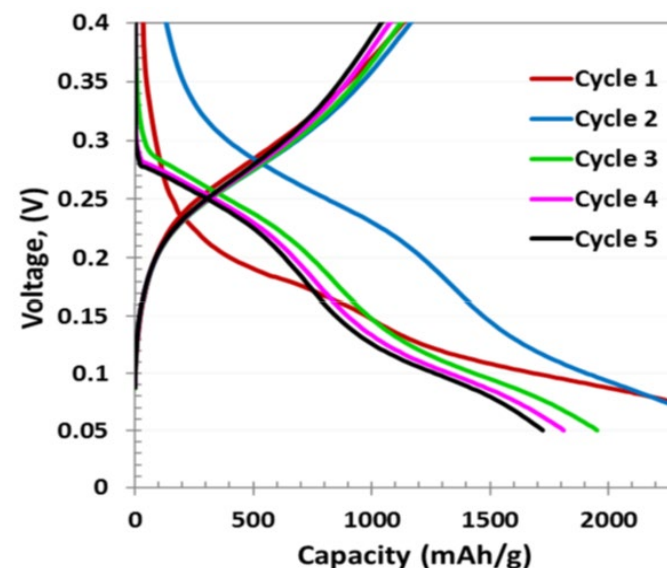


SILICON DEEP-DIVE UPDATE WITH QUESTION AND ANSWER SESSION

JACK VAUGHEY

U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE
2019 ANNUAL MERIT REVIEW



Project ID BAT388

12 June 2019

OVERVIEW

Timeline

- Start October 1, 2017
- End: September 30, 2020
- Percent Complete: 52%

Budget

- Funding for FY 19: \$3900K

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
 - Cost, Performance and Safety

Partners

- Argonne National Laboratory
- National Renewable Energy Laboratory
- Oak Ridge National Laboratory
- Lawrence Berkeley National Laboratory
- Pacific Northwest National Laboratory
- Sandia National Laboratory

RELEVANCE

Stabilization of silicon-based electrodes leading to successful incorporation into electrochemical cells

The **Silicon Deep Dive Next Generation Anode Program** addresses the cost and performance issues preventing the inclusion of silicon into a commercial lithium-ion cell

- Elemental silicon can theoretically store $> 3500 \text{ mAh/g}$
- BatPac models indicates a silicon-based electrochemical cell coupled with a high-capacity cathode presents a pathway to less than $\$125/\text{kWh}_{\text{use}}$
- Modeling shows that the benefits of silicon inclusion diminish after 1000 mAh/cm^3 (electrode basis) for both cost and energy density. These targets can be reached with $\sim 25\%$ Si (balance graphite) in an electrochemical cell.
- Differences in surface chemistry between silicon and graphite require additives and binders to be tailored to this mixed-active material system.

MILESTONES AND ACTIVITIES

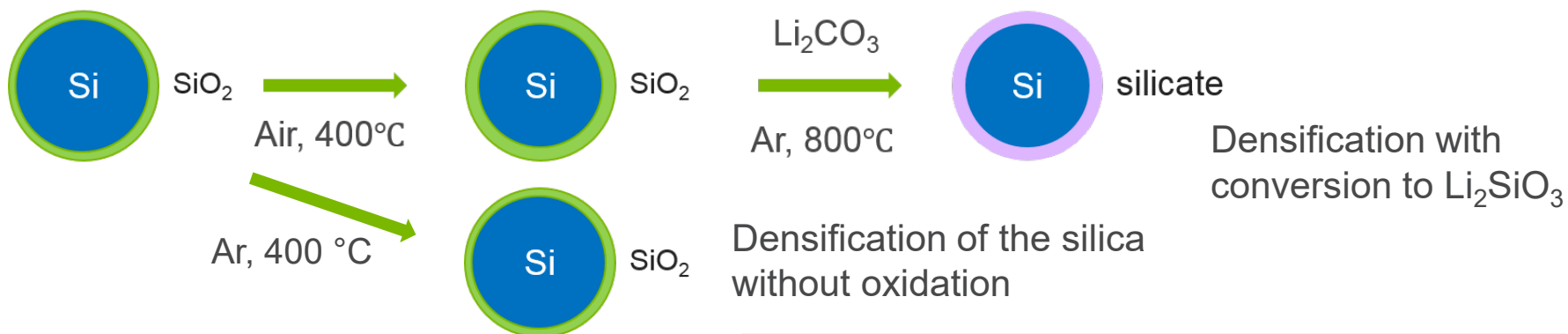
- Q1** Demonstrate improved cycling efficiency of a silicon-based electrode that incorporates either an inorganic or organic surface modification compared to uncoated silicon baseline (*complete*)
- Q2** Exhibit a binder designed to strongly interact with the silicon particle surface that shows enhanced cycling stability versus an LiPAA baseline. (*complete*)
- Q3** Demonstrate that controlling lithium inventory in a full cell can extend cycle life of a silicon-based electrode by at least 10%.
- Q4** Construct and evaluate cells based on optimizing lithium inventory, binder, electrolyte formulation, and testing protocols to achieve a 300 Wh/kg cell design.

Activities

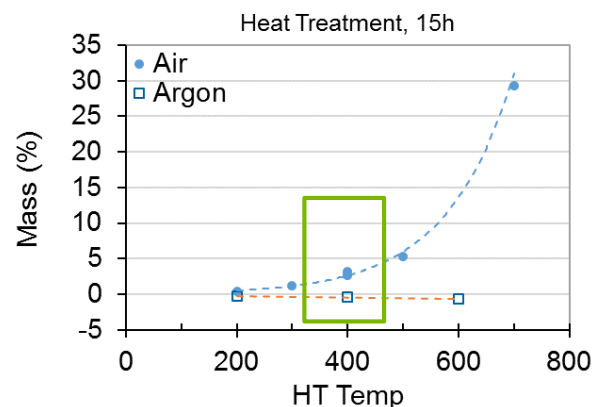
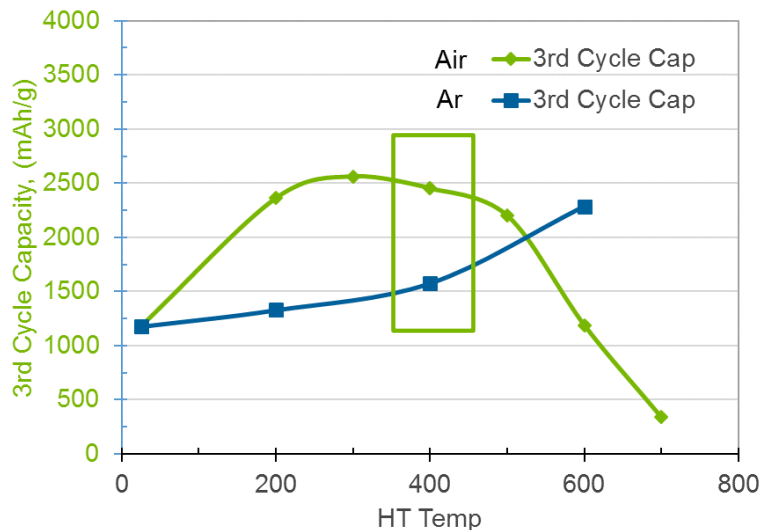
- **Facilities Supporting the Program:**
Battery Abuse Testing Laboratory (BATLab), Battery Manufacturing Facility (BMF), Post Test Facility (PTF), Cell Analysis, Modeling, and Prototyping (CAMP) Facility, Materials Engineering Research Facility (MERF).
- Electrochemical and analytical studies
- Development of coatings, additives, and processes to modify and stabilize relevant interfaces
- Material development (active materials, electrodes, electrolytes, polymers)

MATERIALS DEVELOPMENT

Controlling the Density of Silicon Oxide Coatings



The interfacial layer is critical to performance, SEI formation, and binder processing. In this study the natural SiO_2 layer was densified or modified to form a conductive silicate.

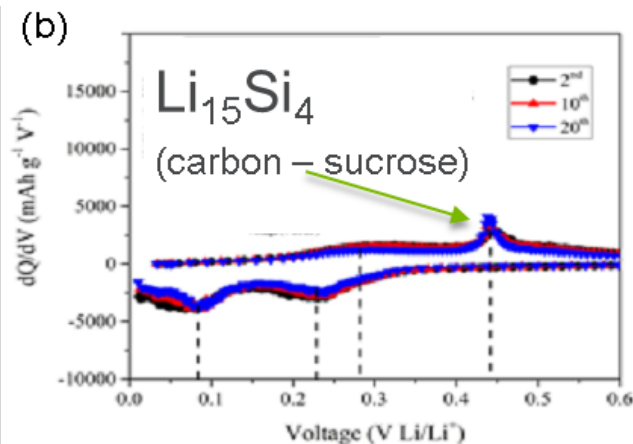
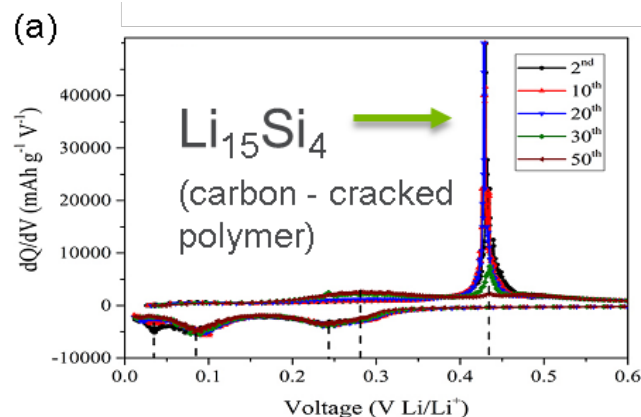


MATERIALS DEVELOPMENT

Silicon Carbon Composite Anodes

Mediating the surface reactivity of silicon during various states of charge is critical to extending cycle life and improving performance. In this study Si NPs were coated with carbons of different crystallinity to assess the role on performance.

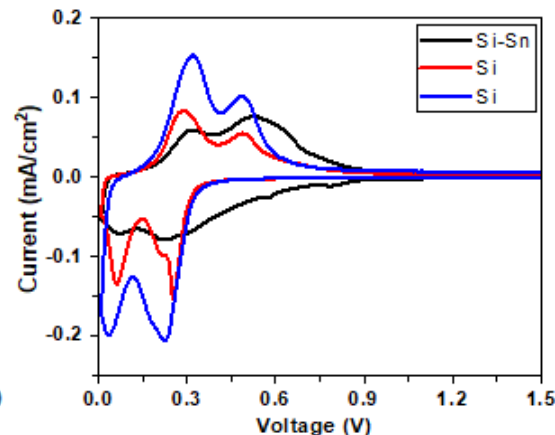
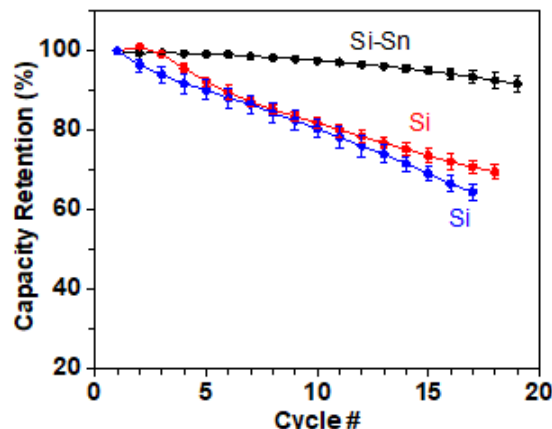
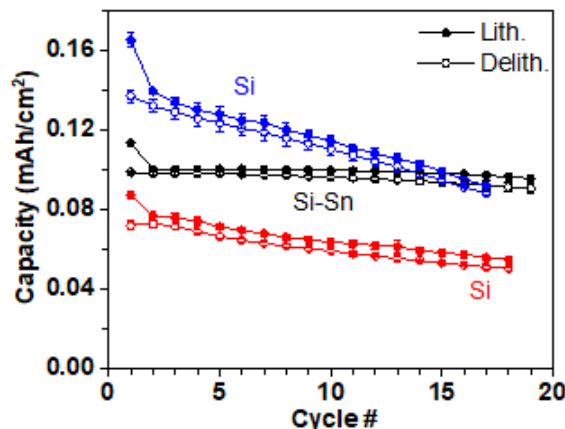
Carbon source: sucrose + heat → disordered carbons
PVDC + heat → conjugated polymer → ordered carbon.



- the cracked polymer derived graphitized coatings deliver higher gravimetric capacity and stable cycling when compared to that of the silicon with a disordered carbon coating
- enhanced cycling of the graphitic cracked polymer derived coatings appear to be associated with initial formation of the crystalline $\text{Li}_{15}\text{Si}_4$ endmember phase.

MATERIALS DEVELOPMENT

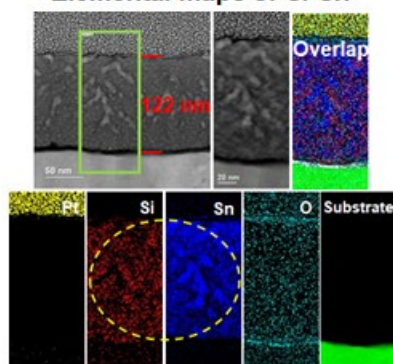
Silicon Tin Composite Anodes



Note: thickness of Si-Sn film falls between Si films

Elemental maps of Si-Sn

Elemental maps of lith. Si-Sn ($\text{Li}_x[\text{Si-Sn}]$)

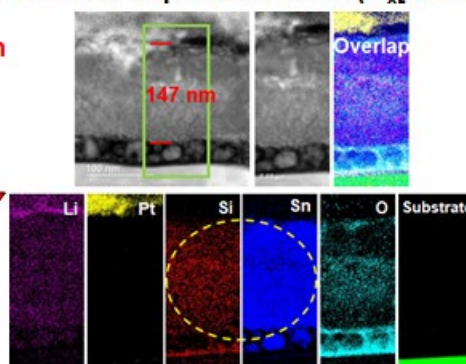


Expansion of Si-Sn

- $t\% = 120\%$
- $\text{vol}\% = 175\%$

vs. Si

- $t\% = 134\%$
- $\text{vol}\% = 246\%$



- Si-Sn films exhibit much improved cycling stability compared to Si films of similar thickness
- Elemental mapping shows dynamic behavior upon lithiation of Si-Sn
- Co-sputtering developed to tune metal species and ratios and probe the physical and electrochemical properties

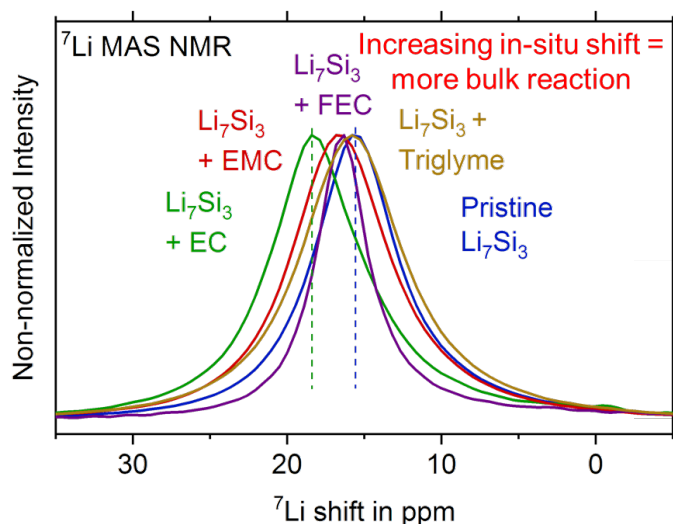
Tong, et al., LBNL

Tong, et al., LBNL

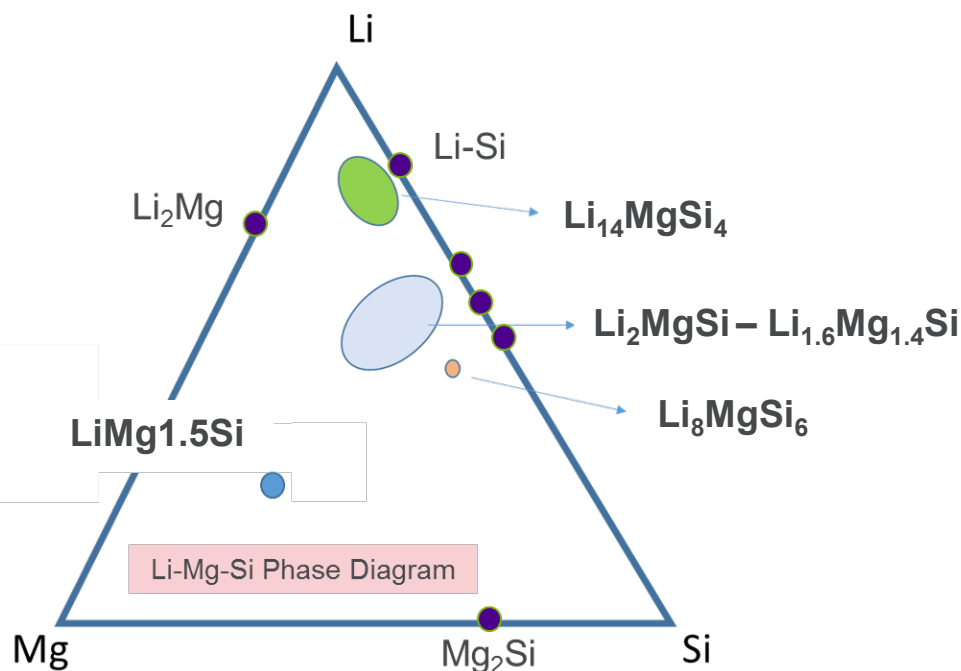
MATERIALS DEVELOPMENT

In-situ Formation of Interfacial Ternary Phases

Previously we identified the redox chemistry of lithium silicides (e.g. Li_7Si_3 ~300 mV) as critical source of **interfacial reactivity**. In the electrolyte reaction we noted the reaction $\text{Li}_{2.3}\text{Si} \rightarrow \text{Li}_{1.7}\text{Si}$ by various techniques including MAS-NMR, XRD, FTIR. More reduced silicides are more reactive.



The products get incorporated into the anode **SEI**, **electrolyte**, or possible **crosstalk** reactions with the cathode. Similar reactions with the **binder** also lead to premature cell failure.



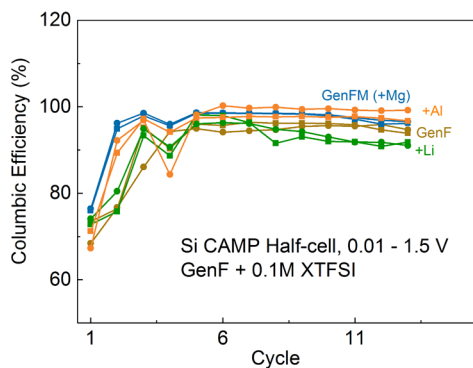
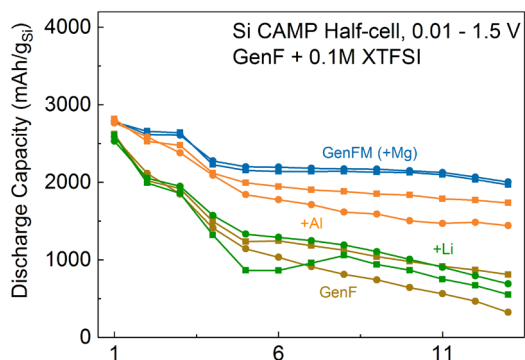
Unlike Li-Si chemistry, little redox chemistry are known for the Mg-containing Zintl phases

MATERIALS DEVELOPMENT

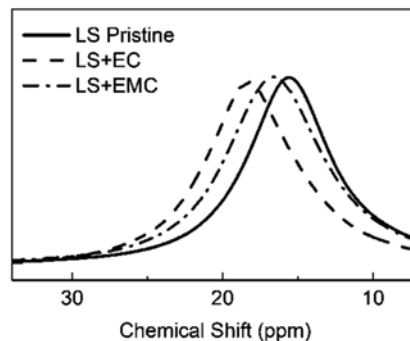
In-situ Formation of Interstitial Ternary Phases

By adding soluble Mg-electrolyte salts to the electrolyte, we observe Mg insertion and formation of ternary Li-Mg-Si Zintl phases at the active electrochemical interface. Using EDX, high resolution XRD, NMR, model compound synthesis we believe the major surface phase is related to $\text{Li}_{14}\text{MgSi}_4$, the electron precise version of $\text{Li}_{15}\text{Si}_4$.

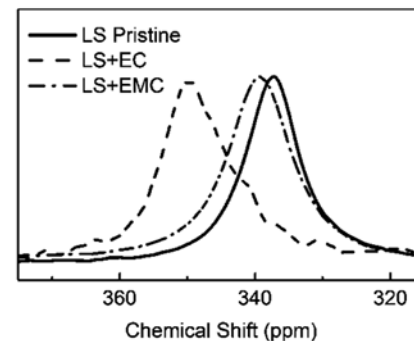
Half cells with CAMP Si electrodes and various salts additives.



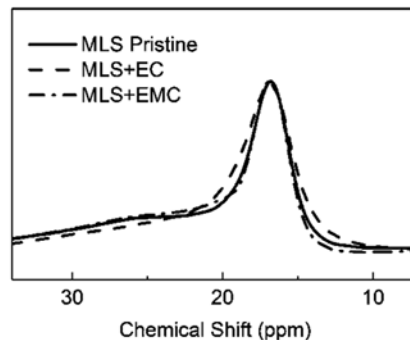
(a) ^7Li MAS NMR



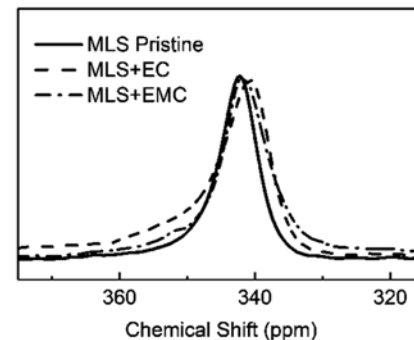
(b) ^{29}Si MAS NMR



(c) ^7Li MAS NMR

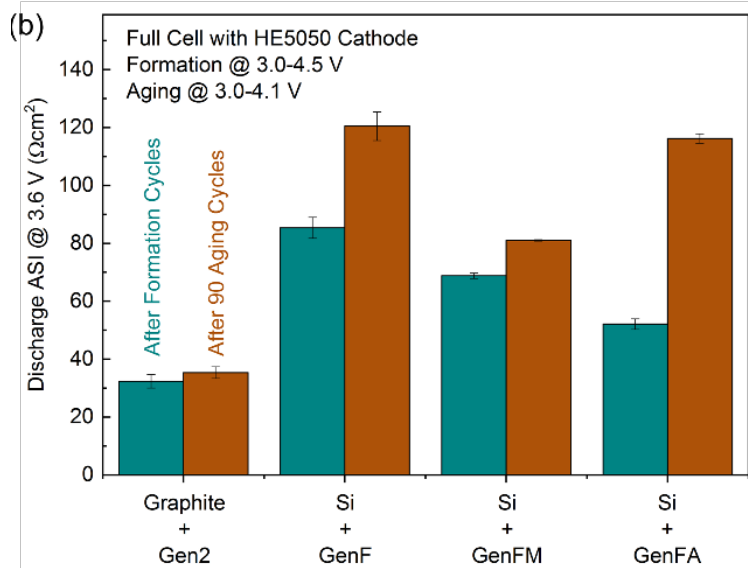


(d) ^{29}Si MAS NMR

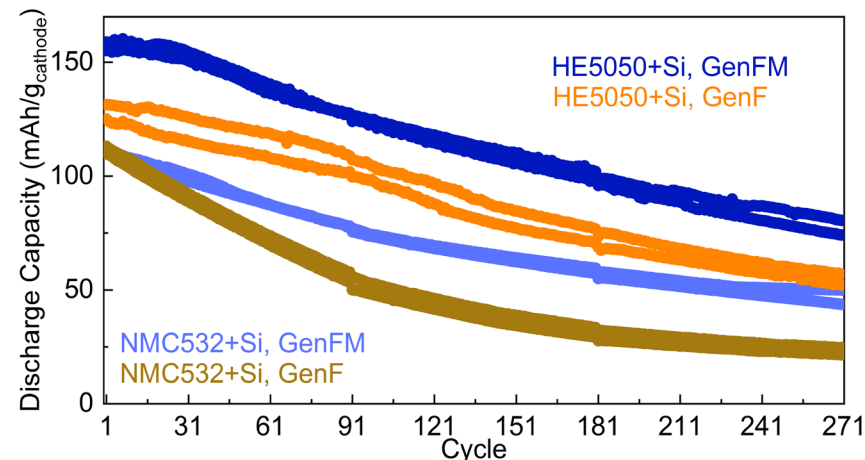


MATERIALS DEVELOPMENT

In-situ Formation of Interstitial Ternary Phases



Impedance – Effect of Additives



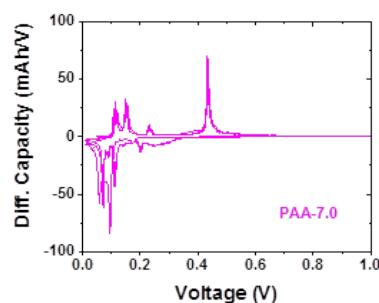
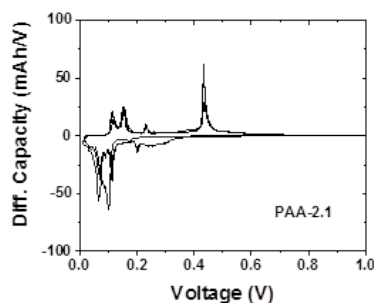
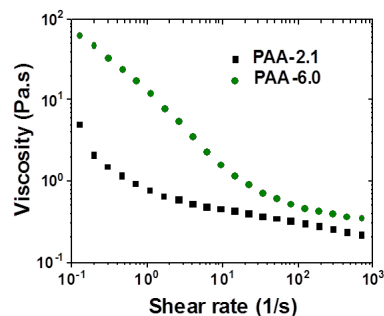
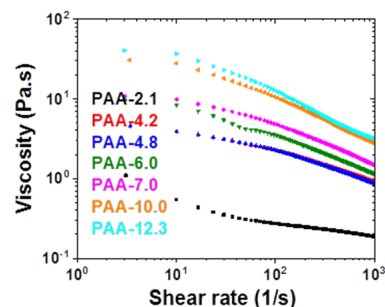
Mg-containing electrolyte showed much higher capacities than baseline even after 270 cycles

- The silicon electrode surface is more stable with the surface Zintl phase. Full window cycling has been done with CAMP electrodes
- Work on role of binder, temperature, and concentration is underway.

INTERFACES

Understanding Baseline PAA Binders

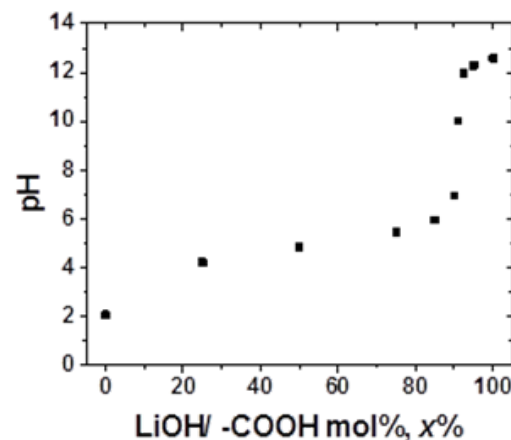
DeepDive electrodes (CAMP) utilize a binder preparation optimized for processing AND performance. However the LiPAA binder system can be utilized over a wide range of pHs depending on LiOH / COOH concentration to make the electrode slurry. In support of



- Lithiation of PAA leads to **stable slurries** but sacrifices the **cycling performance**.
- Avoid increasing pH/Si degradation and undermining the bonding strength.

the need for electrode optimization the role of Li/H ratio for the binder system, viscosity, shear

strength, zeta potential, and performance were evaluated with silicon electrodes.

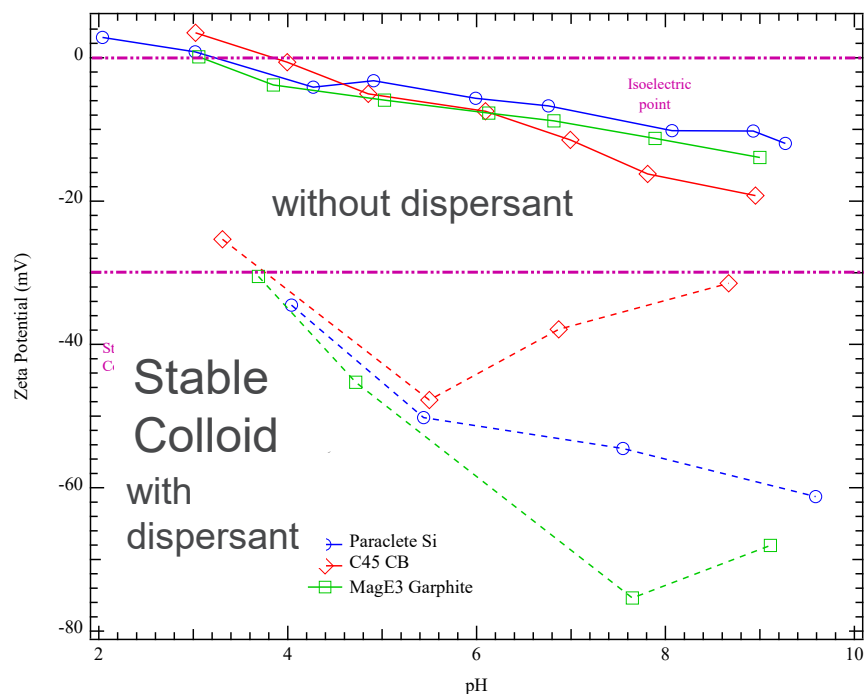


pH is tied to surface functionality

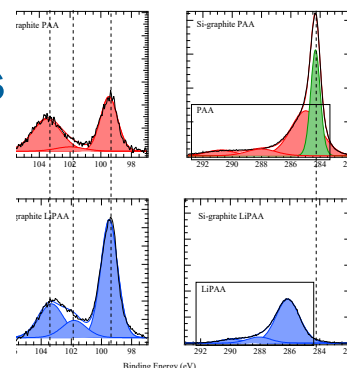
Competing factors that affect stability of slurries and cycling performance have been examined and more variables may be balanced to isolate alternative compositions.

INTERFACES

Understanding Baseline PAA Binders



Zeta potential points to differences in surface chemistry with pH and indicate ways to stabilize the slurry. Using dispersants, electrode formulation and cycling performance can be improved.

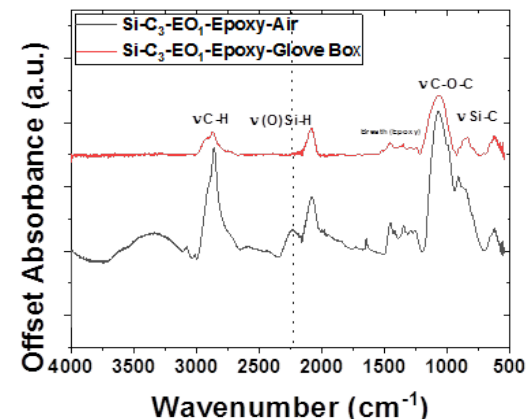
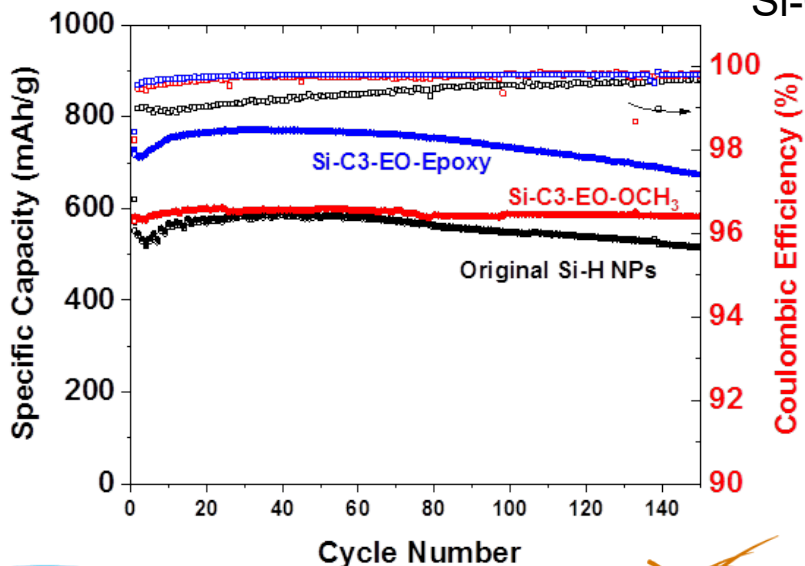
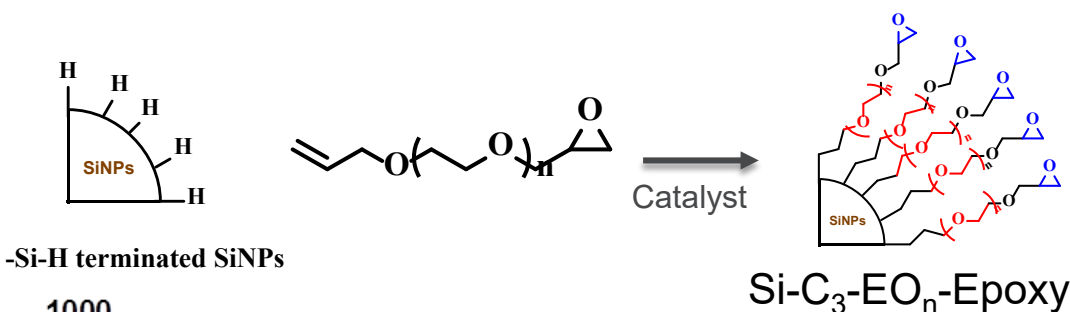


XPS data shows PAA selectively binds to Si while LiPAA binds selectively to graphite. Developed method to quantify binder adsorption on different components. **LiPAA binder doesn't adsorb to Si.**

INTERFACES

Surface Functionalization

The surface of silicon is passivated by silica. Changing the surface to a more reactive species, such as hydride, allows for a more directed surface functionalization to be accomplished.

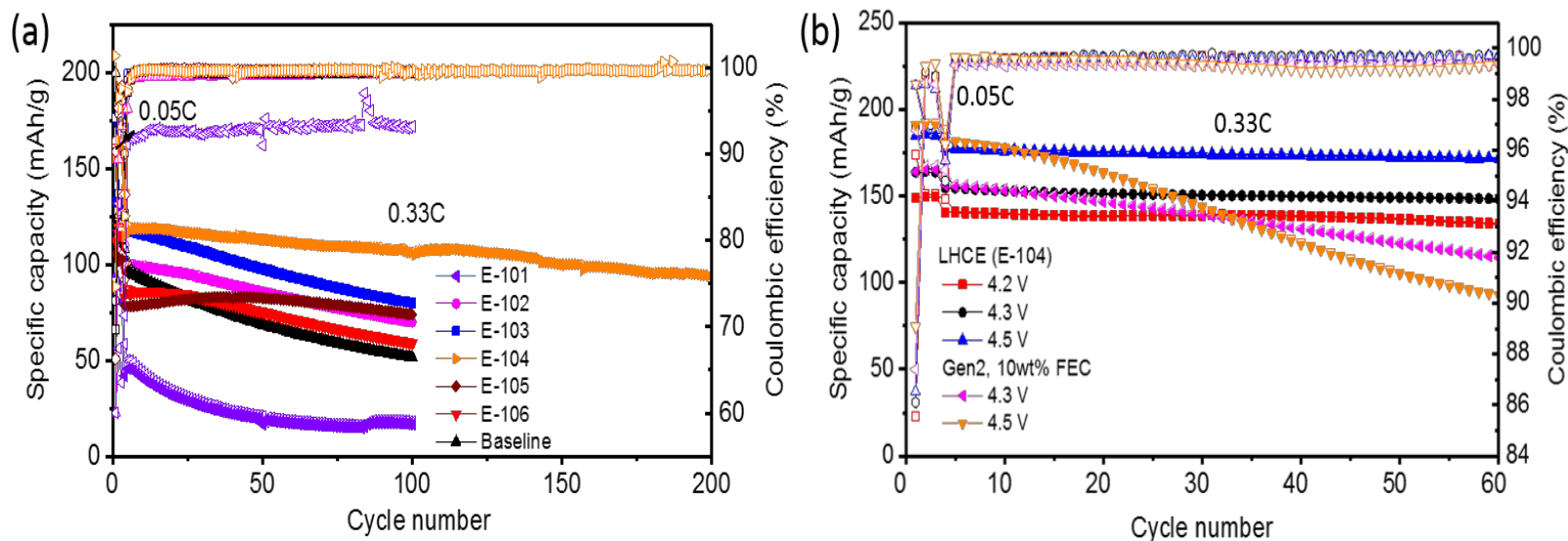


- Surface functionalization improves the cycling stability of SiNPs, for both oligo(ethylene glycol) and EO-Epoxy SiNPs.
- Epoxy-functionalized SiNPs delivers higher capacity due to the improved adhesion to the current collectors (no peeling).

INTERFACES

Concentrated Electrolytes

LiFSI-based localized high concentration electrolytes (LHCEs) with EC-EMC have been developed for Si anodes. Electrolytes with different salt concentration were screened and the results with 1.8M salt gave the best performance. Screening studies indicate that the solvent and diluent (BTFE) molar ratio can be optimized for the best performance. With CAMP NMC532|| Si/Gr cells, the 1.8M LiFSI system demonstrated superior long-term cycling performance with the capacity retention of 81.8% after 200 cycles.



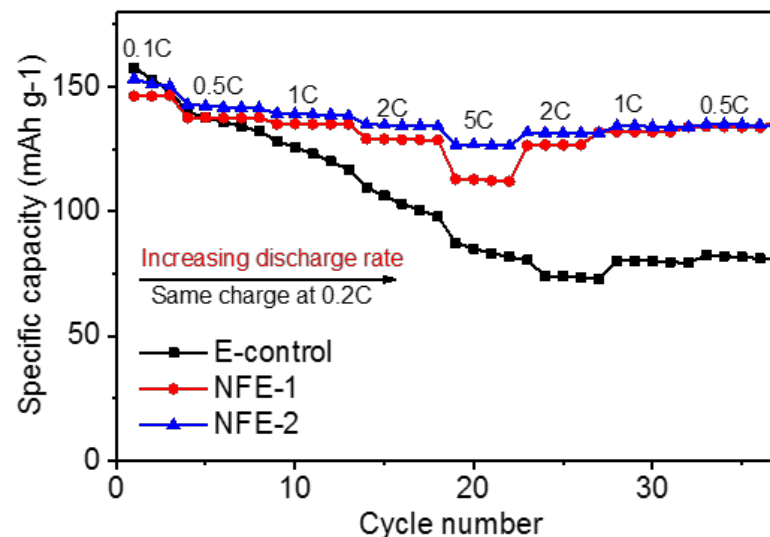
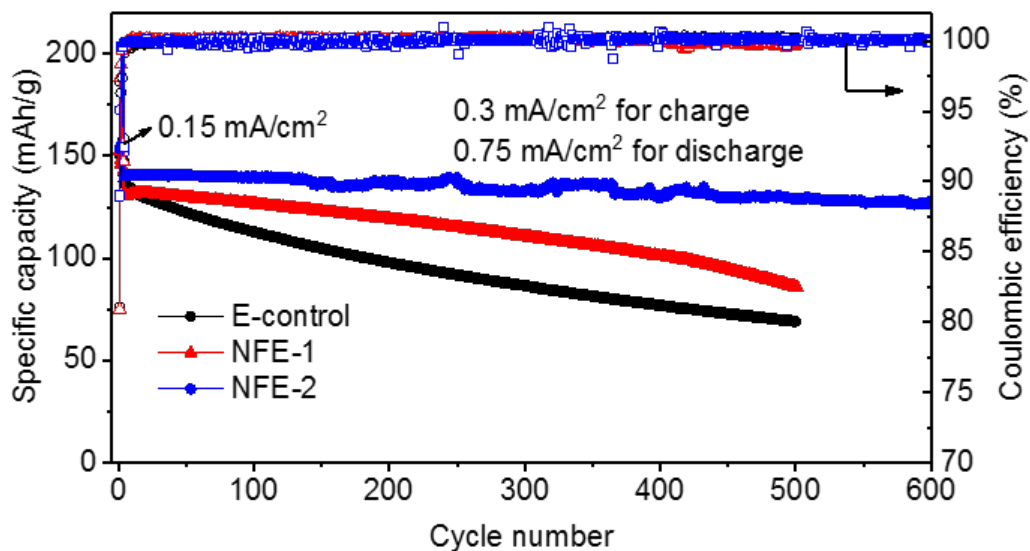
a) Cycling performance of NMC532|| Si/Gr (CAMP electrodes) in BTFE-based electrolytes with different salt concentrations; b) high voltage stability of NMC532|| Li in 1.8M and baseline electrolytes.

Zhang, et al., PNNL

INTERFACES

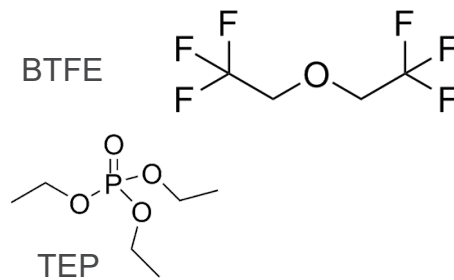
Concentrated Electrolytes

Non-flammable LiFSI-TEPa based electrolytes with (NMC333//Si/Gr full cell)



- E-control: 1.2 M LiPF₆ in EC-EMC (3:7 by wt.) +10 wt.% FEC
- NFE-1: 1.2 M LiFSI in TEP/BTFE (1:3 by mol)
- NFE-2: 1.2 M LiFSI in TEP/FEC/BTFE (1.2:0.13:4 by mol)

➤ Full cells with NFE-2 demonstrated more than 90% capacity retention in 600 cycles, good rate capability and least voltage polarization.

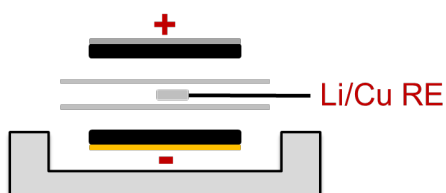


EVALUATION

Silicon Carbon Composite Anodes

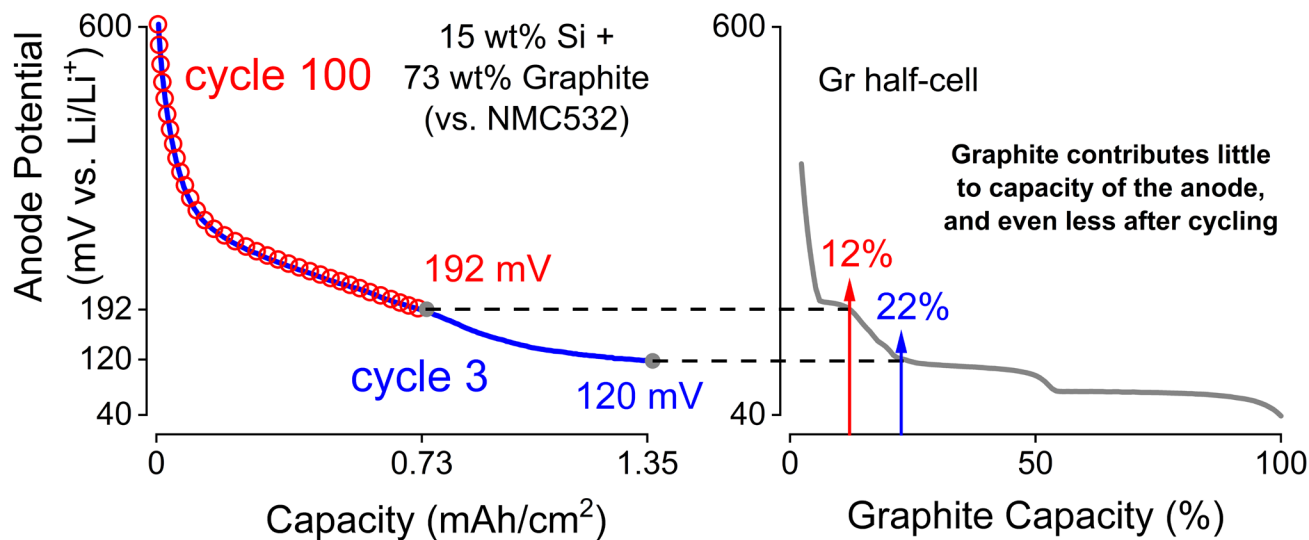
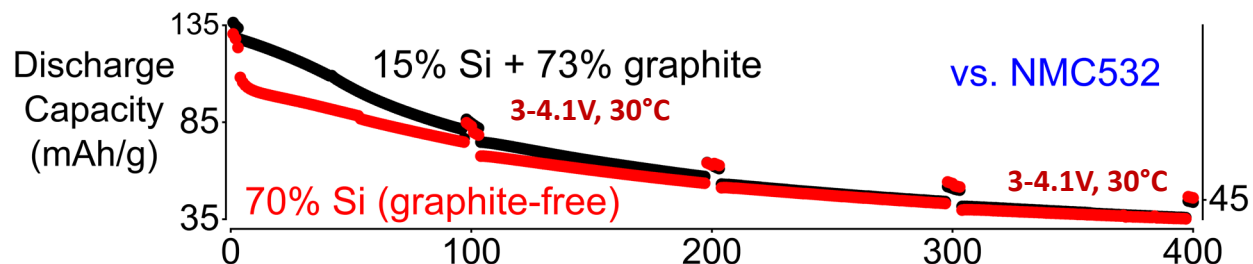
Observation: only a small fraction of graphite capacity is accessed in Si-Gr full-cells during the initial cycles, and the fraction decreases with capacity fade

3-electrode cell



20.3 cm² electrodes
25 μm reference wire
10 wt% FEC electrolyte

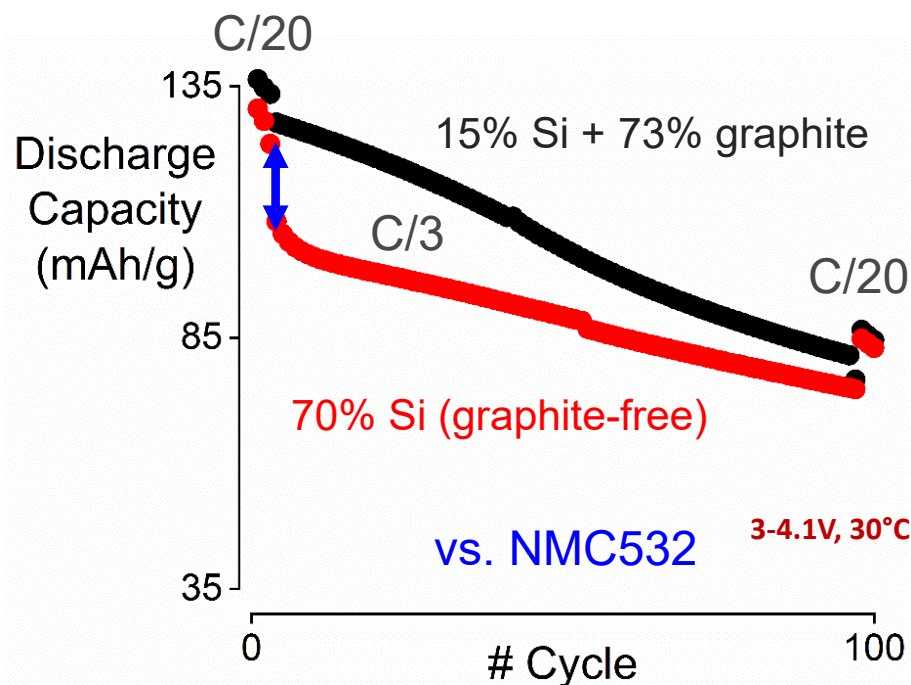
Consequence: after some loss in capacity, only Si stores charge and fade rate is independent of graphite content



EVALUATION

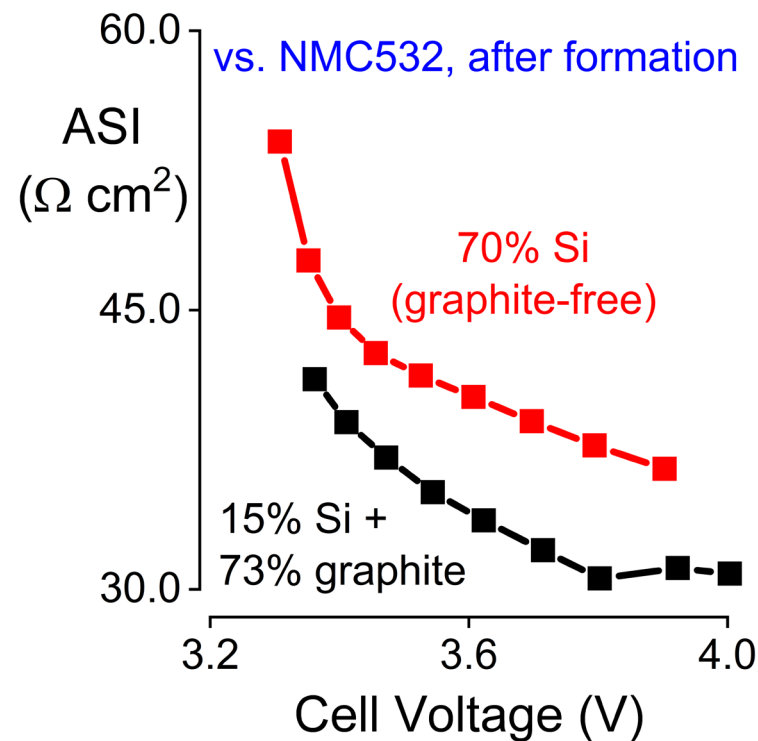
Silicon Carbon Composite Anodes

Higher-Si electrode delivers lower capacity at higher rates



Comparing 15% Si Cells to 70% Si Cells in three electrode cells.

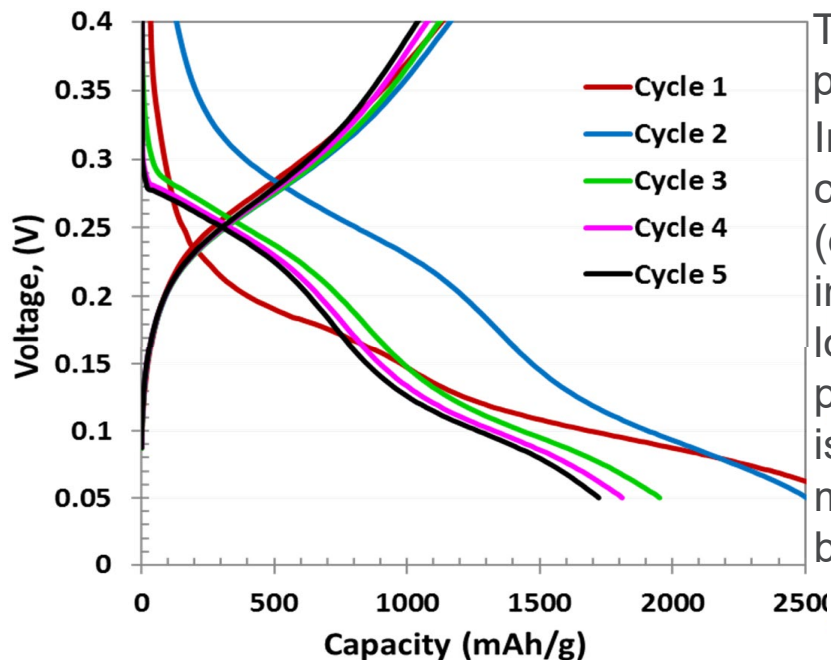
This is a consequence of higher initial impedance



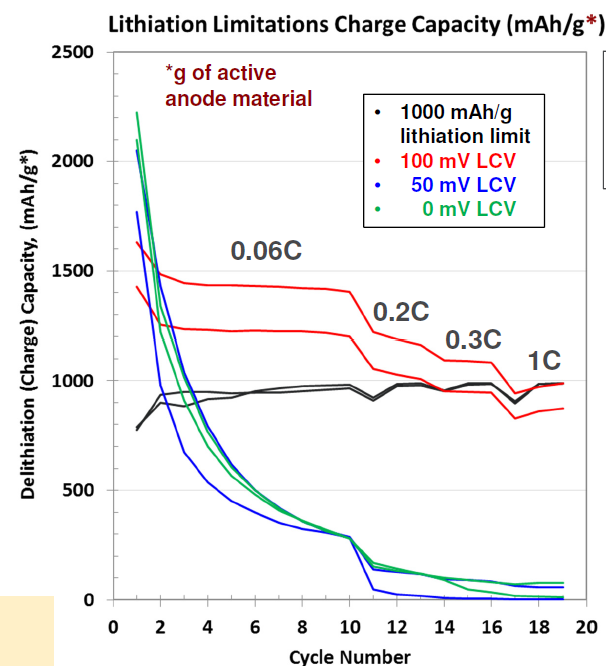
When increasing the silicon content of anodes, sufficient carbons should be added to maintain electronic percolation in the electrode

EVALUATION

Graphite Free Silicon Anodes



The voltage window can be used to control silicon particle expansion. Cell voltage lower by ~200 mV incorporating other carbon materials (e.g., hard carbon) instead of graphite lowers the voltage plateau as graphite is not available. It may enable other binder systems



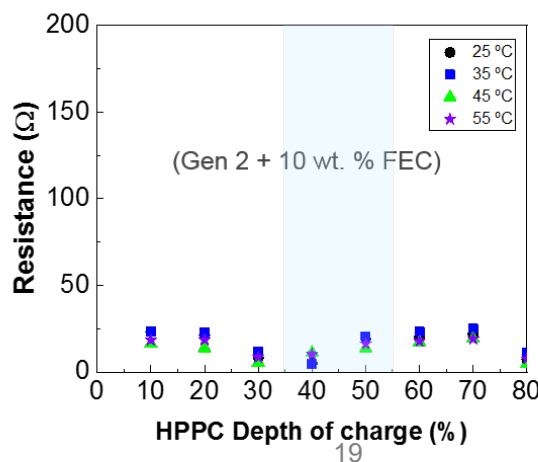
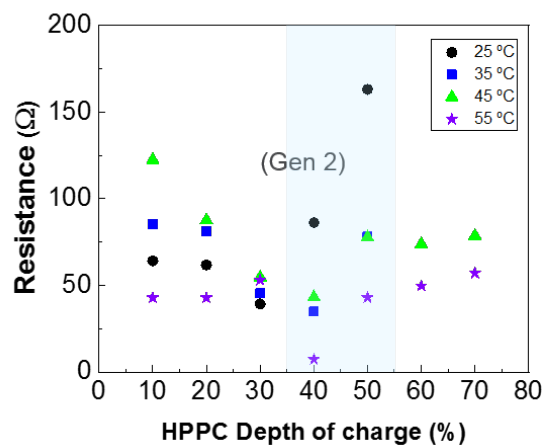
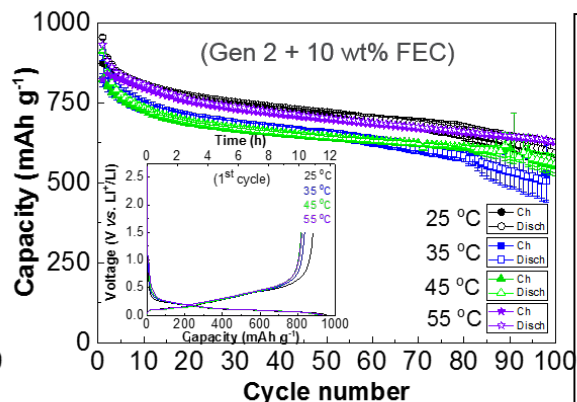
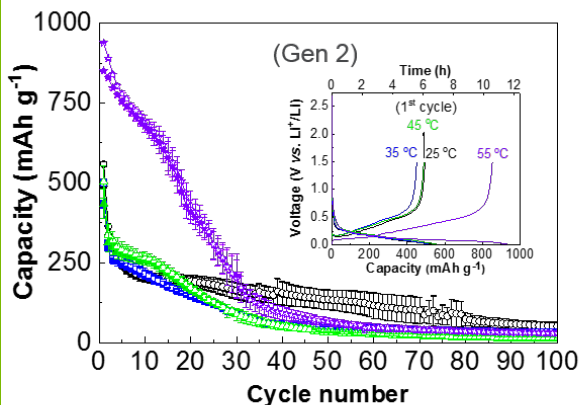
- Clear advantage exists in limiting the extent of lithiation.
- 0 and 50 mV cutoffs result in almost identical fade rates.
- Limiting lithiation to 1,000 mAh/g would require capacity termination rather than voltage termination in full cells.

Dunlop, Trask, Jansen, CAMP ANL

EVALUATION

Role of Temperature

Temperature effects can be significant in the performance of most LIB systems. In Si-based cells, the use of additives, SEI instabilities, and Li-Si phase chemistry all are strongly affected by temperature.



- Si-Gr cells: performance vs temperature varies with and without FEC.
- Temperature (T) affects capacity fade when no FEC is added to the electrolyte. For non-FEC containing cells, the observed capacity differs with T, due to changes in cell resistance.
- Similar cycle-lives and capacities are observed in presence of FEC, suggesting similar mechanisms. FEC incorporation to the electrolyte significantly reduces the resistance of the cell as well as the sensitivity to temperature.

Half cells (vs. Li⁺/Li)

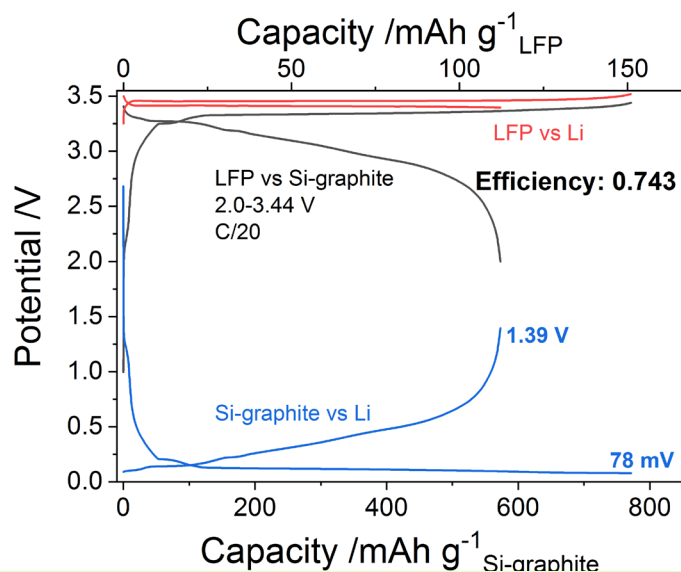
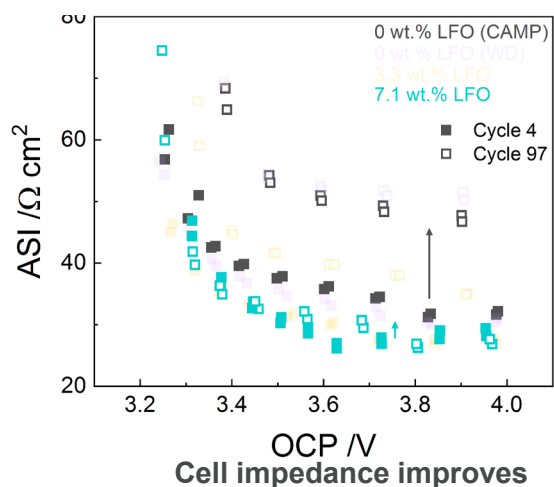
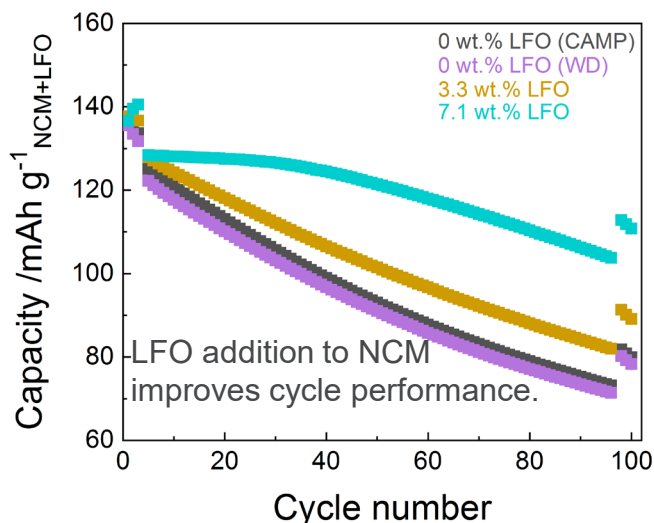
$$\Delta V = 0.01 - 1.5 \text{ V vs. Li}^+/\text{Li}$$

Piernas Munoz, Bloom, et al., ANL

EVALUATION

Role of lithium content

Much of the irreversible capacity in a lithium ion cell containing silicon happens on to first cycle due to SEI formation and irreversible reactions. One strategy to offset this loss is by addition of a one time lithium source to the system (cathode or anode).



% irreversible capacity from active lithium loss on 1st cycle = **92.5%**

Offsetting the loss of lithium due to cell reactions can dramatically improve the CE and extend cycle life. Studies highlight that this strategy works by adding additional lithium to the cell and delaying cell failure.

CONCLUSIONS

The EERE-VTO Deep Dive Silicon Project represents a cross-laboratory collaborative project that seeks to better understand the requirements to successfully develop a silicon-based electrode that meets DOE EERE VTO goals.

- The role of the programs baseline PAA binder has been investigated by a multi-lab team. Research highlights that the parameters that yield the best slurries can damage the surface of the silicon and effect binder bonding strength. The use of a mixed material anode (Si/Gr) has implications for binder choice and the role of processing as the LiPAA prefers PAA while Gr prefers LiPAA.
- A multi-lab collaboration has utilized a novel process to make hydride terminated silicon that is a superior starting material for surface functionalization yielding new materials with better surface control and improved performance.
- A new class of electrolyte additives has been developed that redox-deactivates the surface while allowing good ionic conductivity. The interfacial magnesiated material formed has been found to work with a variety of electrolytes and silicon samples.
- Use of concentrated LiFSi-based non-flammable electrolytes has been identified as a pathway to stable cycling for high volume expansion Si-based anode systems. Addition of a diluent and higher molarity EC/EMC electrolyte increases CE and decreases first cycle losses.

FUTURE WORK

- Continue our study of the interplay of modified surfaces, electrolyte additives, binder stability, laminate properties, and electrochemical cycling as a route to improve our understanding of silicon-based electrodes and provide a path to meet EERE VTO goals.
- Devise and create new interfacial modifications of the silicon surface that add stability and performance to the electrode structure
- Utilize advanced characterization techniques to see how changes to the electrode structure can be detected, modeled, and understood to improve performance.
- Continue collaboration with SEISta team and work to incorporate their insights and effort into full cells.

CONTRIBUTORS AND ACKNOWLEDGMENT

Research Facilities

- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

Contributors

- | | | | |
|---------------------|-----------------------|----------------------------|--------------------|
| ▪ Daniel Abraham | ▪ Sang Don Han | ▪ Michael Liu | ▪ Adam Tornheim |
| ▪ Ira Bloom | ▪ Kevin Hays | ▪ Gao Liu | ▪ Wei Tong |
| ▪ Su Ahmed | ▪ Andrew Jansen | ▪ Wenquan Lu | ▪ Stephen Trask |
| ▪ Nasim Azimi | ▪ Sisi Jiang | ▪ Maria Jose Piernas Muñoz | ▪ Jack Vaughey |
| ▪ Beth Armstrong | ▪ Haiping Jia | ▪ Jagjit Nanda | ▪ Gabriel Veith |
| ▪ Chunmei Ban | ▪ Christopher Johnson | ▪ Nate Neale | ▪ Qingliu Wu |
| ▪ M. Katie Burdette | ▪ Kaushik Kalaga | ▪ K. Nie | ▪ Yimin Wu |
| ▪ Anthony Burrell | ▪ Baris Key | ▪ Bryant Polzin | ▪ Kang Yao |
| ▪ Saida Cora | ▪ Joel Kirner | ▪ Krzysztof Pupek | ▪ Ji-Guang Zhang |
| ▪ Jaclyn Coyle | ▪ Robert Kostecki | ▪ Marco-Tulio F. Rodrigues | ▪ Linghong Zhang |
| ▪ Dennis Dees | ▪ Dave Kim | ▪ Rose Ruther | ▪ Lu Zhang |
| ▪ Fulya Dogan | ▪ Gregory Krumdick | ▪ Niya Sa | ▪ Zhengcheng Zhang |
| ▪ Wesley Dose | ▪ Bob Jin Kwon | ▪ Yangping Sheng | ▪ Tianyue Zheng |
| ▪ Alison Dunlop | ▪ Xiaolin Li | ▪ Youngho Shin | ▪ Ting Zhang |
| ▪ Binghong Han | ▪ Chen Liao | ▪ Seoung-Bum Son | |
| | ▪ Min Ling | ▪ Caleb Stetson | |

Support for this work from Battery R&D, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Brian Cunningham, Steven Boyd, and David Howell